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To: Dr. D. Mills
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EFFICIENCY IMPROVEMENT IN FLUORESCENT LAMPS BY ISOTOPIC TAILORING OF MERCURY

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Lighting uses about 19% (or 22.8 TWh/a) of the electricity generated by Ontario Hydro. Recent research indicates that isotopically tailoring the mercury used in fluorescent tubes can improve the light output by approximately 5%. This improvement has the potential to save approximately 85 MW or $21M of electricity per year. Methods to perform the isotope separation are discussed and recommendations are made for further work.

INTRODUCTION

Interest within Ontario Hydro on energy conservation has led to the examination of energy use in industrial and commercial sectors. Fluorescent lamps, both industrial and commercial, are a significant load on the system, and increasing the output efficiency of these lamps can decrease system demand. Reports from various U.S. groups have shown that tailoring the abundance ratios of mercury isotopes increases the output efficiency of fluorescent lights up to approximately 5% /1/. The explanation for this observation is that adjusting the concentration of Hg-196 improves the efficiency of delivering the 253.7 nm photons to the phosphors on the lamp wall. The following section discusses the economic benefit for Ontario Hydro in improving fluorescent lamp efficiency. The section after that discusses methods for mercury isotope separation, and the final section recommends work for the next stage. Appendix I gives a brief description of the operation of fluorescent lamps and Appendix II describes the photophysics behind the efficiency improvement.

ECONOMICS

Studies on isotopic tailoring of mercury indicate that fluorescent lamps containing mercury enriched to 2-3% in Hg-196 have about a 5-7% increase in light output. Ontario Hydro produces about 120 TWh/a, of which lighting accounts for 18.5% (or 22.8 TWh/a) of total generation. Fluorescent lamps account for 60% (or 14 TWh/a) of the total lighting load /2/. We assume that a 5% increase in lamp efficiency translates to a 5% decrease in power consumption. This 5% decrease amounts to 0.7 TWh/a

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or 0.57% of total annual generation, or 11% of a 750 MW reactor. If we assume an electricity cost of $0.03 per kWh, then the saving in energy amounts to $21M per year for Ontario.

The assumption that increased light output leads to lower demand is valid only if there is widespread use of these lamps. Discussions with fluorescent lamp manufacturers have indicated two possible lamp types that can be produced:

a) Standard 40 W lamps can be produced with isotopically tailored mercury. No design changes are necessary, but the lamps will be 5% brighter than those made with natural mercury. These lamps can be used in new installations which will have 5% fewer lamps, or in existing large industrial or commercial installations which can remove 5% of their lamps, and still have the same brightness at the work surface.

b) By modifying the electrodes, lamp diameter or inert gas pressure and composition, new lamps can be designed to operate at lower power and use existing fixtures and ballasts, but produce the same brightness as standard 40 W lamps. The Watt-Miser™ lamp, for example, is already on the market. It operates in a standard fixture with a standard ballast but consumes only 34 W of power; the drawback is that it is not as bright as a 40 W lamp. These new lamps would be used in smaller installations, such as homes, apartment buildings and offices where reducing the total number of lamps is not practical.

The optimum market penetration will be a mix of options and will depend on analysis of market requirements.

Using the estimated value of 14 TWh/a for fluorescent lighting, and assuming there are 8000 hours per year, then 1700 MW are used on lighting. Assuming an average size of 40 W per fluorescent lamp gives an estimated 40 million lamps in the province. The estimated lifetime of these lamps is ~16,000 hours, and assuming a 12 hour duty cycle per day, the lamps must be replaced every 4 years, or roughly 10 million lamps per year. General Electric Canada has reported that the lamps are filled with approximately 50 mg of mercury; the lamps do not operate properly if they contain less than 30 mg mercury. Therefore, to fill the 10 million lamps required for replacement uses about 500 kg of mercury per year.

If we assume that approximately one-half the annual electricity savings are available for isotope separation, then about $10M can be spent. If 500 kg of mercury are required per year, then we could spend up to $20 per gram for isotope separation to produce mercury enriched to 2% in Hg-196. Another way to look at the problem is that if we could produce mercury enriched to greater than 90% Hg-196, then this material could be mixed with natural mercury to produce 2% Hg-196. If mercury containing 90% Hg-196 was available, then approximately 20 g would be needed per kilogram of natural mercury to increase the concentration to 2%. At this rate, 11 kg of highly enriched mercury are required per year, at a value-added cost of $900 per gram. (In other words, it could cost up to $900 to produce 1 gram of highly enriched mercury, and Ontario Hydro would still save money.) For comparison, uranium is enriched by AVLIS (Atomic Vapour Laser Isotope Separation) at a cost of $140/kg and by thermal diffusion at $500/kg /3/. Uranium is difficult to vaporize and, therefore a significant portion of the cost for each method is for the vaporization step. Mercury, on the other hand, vaporizes easily and thus it should be possible to achieve enrichment costs comparable to those for uranium.

SEPARATION METHODS

Mercury has seven naturally occurring isotopes. The atomic weights and percent abundances are given in Table I below.

TABLE I

NATURAL ABUNDANCES OF THE ISOTOPES OF MERCURY

Isotope	Abundance (atom %)	Isotope	Abundance (atom %)
196	0.146	201	13.22
198	10.02	202	29.80
199	16.84	204	6.85
200	23.13		

Three methods are recorded in the literature to separate Hg-196 from natural mercury.

1. The first method is thermal diffusion. A note by Groth and Harteck /4/ has indicated that they used a thermal diffusion tube of moderate length (2.2 m) to enrich mercury vapour by 0.5 parts per thousand, at a production rate of 0.25 g per hour. They reported this work in 1939 and they do not give any further information on the actual enrichment that they obtained. Making some assumptions on composition, it appears that they increased the Hg-196 concentration from 0.146% to 0.17% atom percent, or 16% enrichment.

2. A second method has been proposed by Webster and Zare /5/ in which they use a mercury lamp, containing Hg-196 to excite the Hg-196 component of natural mercury vapour. The excited atoms react with HCl in the presence of butadiene to form mercury chloride. They report the final Hg-196 enrichment to be 4.2. (The enrichment is defined as the atom percent Hg-196 in the product divided by the atom percent in the feed.) This enrichment implies that the atom percent Hg-196 in the product is 0.6%. The production rate is low (~2 mg/h), however. More recently, a Russian paper /6/ has discussed modifications to the method in which oxygen is substituted for the hydrogen halide. They produce Hg-196, with an annual production "sufficient for the Soviet domestic market"; they do not give any indication of the size of this market.

3. The third method, AVLIS, consists of a source of mercury vapour, a laser to selectively ionize the isotope of interest, and an extractor to remove the ionized atoms /7/. The method has been demonstrated for uranium separation, and a report from Lawrence Livermore National Laboratory has outlined a method for using AVLIS for mercury isotope separation. This report did not give any experimental results on the enrichment for Hg-196.

RECOMMENDATIONS

Given the potential large annual saving for Ontario Hydro by using isotopically tailored mercury, further work is called for. Of the three methods proposed for isotope separation, thermal diffusion has the best low-cost potential because it is a "low tech" solution, and similar units are already in commercial use for separating other isotopes. The mercury lamp method of Webster and Zare is the next most complex. The operating procedure is straightforward, but the requirement for chemical conversion (mercury chloride to elemental mercury) at each stage makes it unattractive for large-scale

application. The laser method, AVLIS, is the least desirable for the first attempt because of the much greater complexity of the method, and therefore large inherent operating cost.

GTE, one of the major fluorescent lamp producers in the U.S., is examining isotope separation by using mercury lamps (method 2 above) and have rejected AVLIS because of cost (see Appendix III). They also reject thermal diffusion because they have noted a degradation of UV production efficiency if the other isotopes are significantly changed from their natural ratios. The requirement that the remaining mercury isotopes be unchanged suggests that any isotope separation method which can produce mercury enriched to greater than 90% Hg-196 can be considered. Thus, using a thermal diffusion column to produce 2% Hg-196 is not practical, because the lamp efficiency is degraded with this mercury. On the other hand, if thermal diffusion can produce highly enriched Hg-196 at reasonable cost, then the method is attractive. Distillation has not been mentioned in the literature, but since the Science Section has considerable expertise in this field, we should evaluate the suitability of the method to produce highly enriched mercury.

The next step in this investigation is to evaluate possible isotope separation methods, and to make a recommendation for further testing. This will lead to a proposal for a program to produce enriched mercury and to test the light output of efficiency fluorescent lamps using this mercury. We expect to work closely with industry in the lamp testing stage of such a program.

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APPENDIX I

FLUORESCENT LAMPS

Figure 1 illustrates the main processes occurring in a fluorescent lamp. Electrons collide with mercury atoms and excite the atoms to the 6^3P_1 state (Fig 1a). There is a certain probability that an excited atom collides with a ground state atom and is transformed into an adjacent state (Fig 1b). Transitions from these states to the ground state are forbidden, with the result that the excitation energy is lost. Ideally, the atom emits a photon which leaves the gas and strikes the phosphor (Fig 1c). The photon excites the phosphors, which in turn emit a spectrum of visible light (Fig 1d).

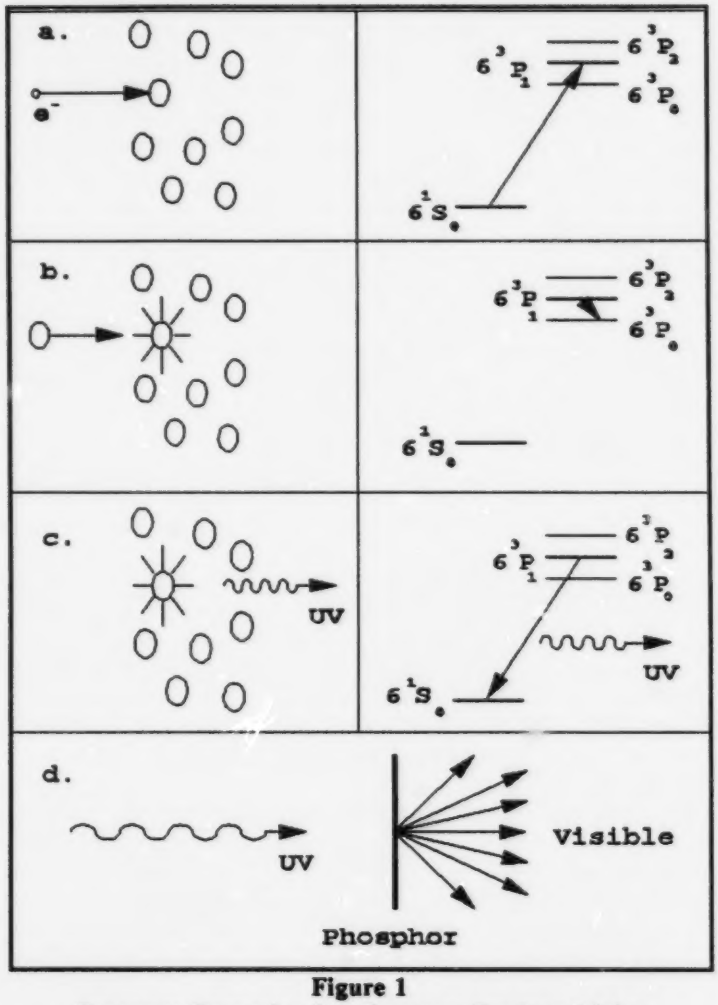

Figure 1
Processes Occurring in a Lamp to Produce Light.
(a) Collision with electron produces excited atom. (b) Collisional deactivation. (c) Excited atom emits a photon. (d) UV photon strikes phosphor to produce visible light.

A fluorescent lamp consists of three parts--(a) a glass tube with electrodes sealed in the ends, and filled with mercury and inert gas, (b) a ballast, and (c) a starter /8/. The glass tube is coated with phosphorescent materials that respond to the 253.7 nm line emitted by mercury atoms to produce light. By choosing a mixture of phosphors, the spectrum of emitted light can be made to approximate natural light. The tube is filled with about 50 mg of mercury, and then filled with inert gas (argon or neon) to a pressure of a few torr.

When the lamp is turned on, a current warms the electrodes to begin boiling off electrons, and warms the mercury to increase its vapour pressure. The starter circuit provides a voltage pulse to initiate the discharge. Since discharges have a negative voltage and current relationship, the ballast stabilizes the operation against fluctuations in line voltage. For ac lamps the simplest ballast is an inductor. The inert gas serves to lower the potential required to start the lamp, and to increase the probability of collisions between electrons and mercury atoms; these collisions excite the mercury to the 6^3P_1 state.

Fluorescent lamps operate in a rather narrow range of permissible conditions.

A. **Temperature**: Light output increases with increasing temperature to about 40°C and then decreases. This is because the number of photons emitted is proportional to the number density of mercury atoms in the gas phase. At higher temperatures, and hence higher number density, the light output decreases because of radiation imprisonment (see Appendix II). In addition, pressure broadening shifts the emitted photons to longer wavelengths. Since the phosphors are optimized for 253.7 nm light, any shifting of wavelengths decreases the efficiency of light production.

B. **Current**: Increasing the current density increases the number of collisions between electrons and mercury atoms and therefore increases the efficiency of production of excited mercury. If the current density is too high, then other excited states of mercury are also produced. Because the phosphors are not sensitive to the wavelengths produced from these states, energy is wasted and efficiency decreases.

C. **Tube Diameter**: Decreasing the tube diameter increases the current density and, therefore, degrades efficiency (see B). Increasing the diameter too much, however, creates a "dead space" between the discharge and the tube wall. This dead space contains ground state mercury atoms which absorb the emitted photons, and thus decrease the number of photons that reach the walls. The operating temperature also decreases as the diameter increases, and this results in a lower vapour pressure of mercury.

D. **Tube Length**: The voltage drop across the lamp equals the voltage drop across the two electrodes plus the voltage drop across the discharge. The voltage drop across the discharge is responsible for light production. This voltage drop increases with increasing tube length, while the drop across the electrodes is constant. Therefore, increasing the length of the lamp increases the efficiency of converting electrical energy into light, and the length is limited only by the voltage available to drive the lamp.

   Another consideration that links C and D is that while long, fairly wide-diameter lamps may be electrically efficient, the surface brightness degrades. Therefore, a balance has to be found between efficiency and brightness.

E. **Inert Gas Pressure**: If the gas pressure is too low, then the mean free path for electrons is larger than the diameter of the tube, and the electrons arrive at the tube wall without striking a mercury atom. As the pressure increases, the number of collisions increases and the number of excited mercury atoms increases. If the pressure is too high, however, then excited atoms can be collisionally deactivated and electrical energy is converted to heat rather than to light.

APPENDIX II

EFFICIENCY IMPROVEMENT BY ISOTOPIC TAILORING OF MERCURY

Light Emission and Absorption in Mercury Vapour

The efficiency of a fluorescent lamp depends on the characteristics of the lamp itself (see Appendix I), and on the physical processes that occur in mercury vapour. The primary excitation process is a collision between a ground state mercury atom and an electron, which excites the mercury atom to the 6P state, $Hg\ (6^1S_o) \rightarrow Hg^*(6^3P_1)$. In the absence of interferences, the excited atom emits a photon and returns to the ground state. The photon strikes the phosphors, which, in turn, produce visible light. Processes that interfere with the photon before it can reach the phosphor on the walls degrade lamp efficiency, however.

These interferences take two forms in standard fluorescent lamps--radiation imprisonment and collisions.

a) **Radiation imprisonment** explains an apparent lengthening of the lifetime of an excited state; the lifetime is the mean time between absorption and emission of a photon. Measurements on the lifetime of the 6^3P_1, state of mercury show that it is about 1.2×10^{-7} s/9/ when only a small number of atoms are present; decreasing this number has no effect on the lifetime. Increasing the number of atoms, however, increases the measured lifetime. When the number of mercury atoms is the same as in a fluorescent lamp ($\sim 5 \times 10^{-3}$ torr) the lifetime lengthens about 70 times. The reason is that an emitted photon has a certain probability of being absorbed by another mercury atom before it can escape and reach the detector. The probability is equal to the cross section for absorption multiplied by the number density. On average, each photon undergoes between 70–100 absorptions and emissions before it can escape from the mercury vapour. This process of absorption and re-emission, which delays the escape time for a photon, is known as radiation imprisonment. Radiation imprisonment by itself does not necessarily decrease lamp efficiency; however, by trapping the photons in the vapour, the probability for collisional deactivation increases.

b) **Collisions** between excited mercury atoms and either another mercury atom or an inert atom can have one of two results--energy transfer or deactivation.

   i) An **energy transfer** collision occurs between two mercury atoms where the excitation energy of the first atom transfers to the second one. This process is independent of the identity of the two isotopes participating in the collision, in contrast to radiation imprisonment, in which the emitted photons can only be absorbed by atoms of the same isotopic species.

   ii) A **deactivation** collision occurs between an excited mercury atom and any other atom present (ground state mercury or inert gas) and populates states adjacent to the 6^3P_1 state, ie 6^3P_2 or 6^3P_o. Transitions from either of these states to the ground state are forbidden. Therefore, if the atom transforms into either of these states, the energy is lost. This type of collision is the main cause of lamp inefficiency.

Efficiency Improvement

The probability of an excited atom undergoing a deactivating collision is proportional to the collision frequency multiplied by the lifetime of the excited state. The collision frequency depends on the pressure and temperature. The operating temperature of the lamp is fixed and the pressure can not be lowered without decreasing light output (see Appendix I). Improvements in lamp efficiency are

possible only if the lifetime of the excited state can be lowered and therefore the probability for collisional deactivation reduced.

The resonance line of mercury at 253.7 nm consists of five lines, spread over approximately 0.05Å (Figure 2). We can account for these lines as follows. Since there are seven isotopes of mercury, we expect to see seven lines, but the contribution from Hg-196 (at 0.146% abundance) is negligible. The isotopes Hg-199 and Hg-201 have nonzero nuclear spin and their lines are split into a total of five additional lines, which coincidently overlap each other and the line from Hg-204. With collisional broadening the result is five lines in the spectrum.

Examination of the spectrum in Figure 2 suggests two methods to decrease the lifetime of the excited state.

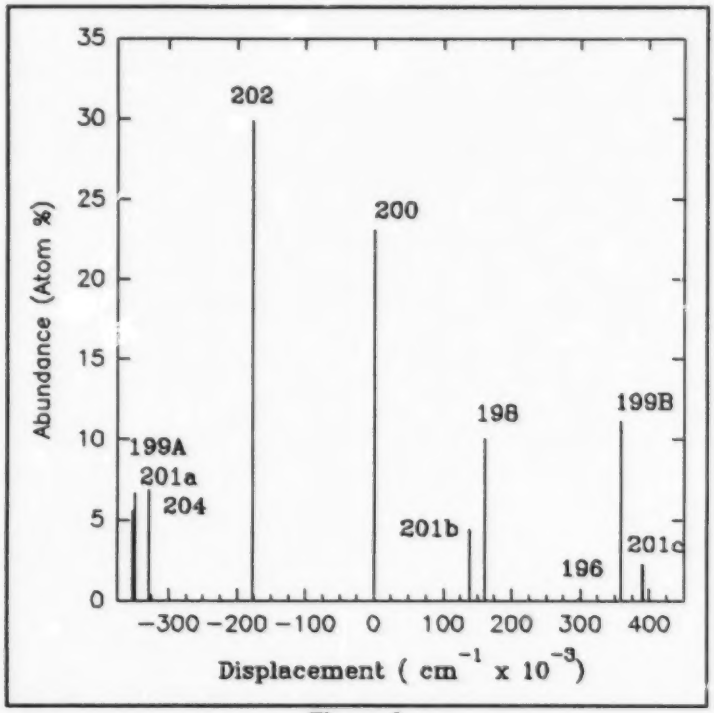

Figure 2
Hyperfine Structure of the Mercury Resonance Line at 253.7 nm.

a) The first method is based on measurements of the lifetime of the excited state of mercury. Suppose the lifetime of one isotope is measured. If additional isotopes are added, while keeping the number density constant, then the lifetime decreases, proportionally to the number of isotopes present (or, proportionally to the number of lines in the spectrum). In natural mercury, the lifetime is one-fifth that of a single mercury isotope. The reason for this decrease is that an emitted photon can only be absorbed by another atom of the same isotopic species or by an atom whose absorption frequency is close to that of the emitted photon. Thus in natural mercury, an emitted photon can only be absorbed by one-fifth of the molecules present. The minimum lifetime for excited mercury occurs when the intensities of all lines in Figure 2 (ie number density x probability of spontaneous emission) are the same. The isotopic tailoring required for this is difficult and most likely prohibitively expensive.

b) The second method to reduce lifetime is based on energy transfer collisions. An experiment to measure the lifetime of Hg-198 showed that the lifetime decreased when trace quantities of Hg-199 and Hg-200 were present/9/. These isotopes provided additional channels to release photons. A photon emitted from Hg-198 can only be reabsorbed by another Hg-198 atom. However, Hg-198 can collide with Hg-199 or Hg-200 and transfer the energy to these isotopes. The probability that a photon emitted by one of these atoms will be reabsorbed is small, because so few of them are present. Thus the photon escapes from the mercury vapour.

Transferring this idea to natural mercury suggests that increasing the concentration of Hg-196 to a few percent should improve light output efficiency. The Hg-196 can receive energy by collisional energy transfer from other mercury isotopes, and because the number density is low relative to the other isotopes, the probability of another Hg-196 atom absorbing the photon is small. Therefore, the net effect is to increase the probability of light output.

Researchers at GTE have found that increasing the Hg-196 concentration to 2-3% increases the light output of a fluorescent lamp by ~5-7%. Further increases in Hg-196 concentration are not useful because at elevated concentrations, significant radiation imprisonment occurs. The other advantage to Hg-196 is that its hyperfine line is not overlapped by other lines. The overlaps on the other mercury lines also suggest that adjusting the concentration of these isotopes is not useful.

The final implication of these results is that if some method were found to split the overlapped hyperfine lines, this would also improve light output. Some work has been done on surrounding the lamps with magnetic fields to induce Zeeman splitting of the lines. It is not known whether this is practical.

APPENDIX III

STATUS OF MERCURY ISOTOPE SEPARATION AT GTE

GTE, one of the major lighting companies in the U.S., has worked in advanced lighting research for a number of years. Since 1983, GTE in collaboration with the U.S. Department of Energy and the Lawrence Livermore Laboratory, has investigated the feasibility of producing an isotopically tailored mercury fluorescent tube.

The work is performed by Dr. Jakob Maya at GTE labs in Massachusetts. During a telephone conversation he mentioned they had performed tests which showed that the distribution of mercury isotopes did affect the efficiency of light output; that is, the best improvement was obtained with 2–3% mercury–196, and the ratios of the remaining isotopes as close to natural as possible. Altering this distribution degraded light output. For this reason, his group had rejected thermal diffusion and ultracentrifuge methods for isotope separation, because they introduce a gradient into the isotopic distribution.

Dr. Maya also mentioned that the main stumbling block at GTE is trying to produce enriched mercury at a cost that will keep their lamps competitively priced. He was quite interested in Ontario Hydro's perspective, since we are concerned with reducing system demand. He seemed to indicate that their process may produce enriched mercury such that the pay back time is about two years, but that they would like to have a pay back time of no more than six months for commercial reasons. He was a little vague on this point (proprietary information?), and I did not pursue the matter.

There seems to be an excellent opportunity for collaboration here, since GTE has expertise in lighting and the manufacture of fluorescent tubes, and Ontario Hydro has expertise in isotope separation.